

## FLAVOR QUALITY IN EXPLOSION PUFFED DEHYDRATED POTATO. 1. A Gas Chromatographic Method for the Determination of Aldehydes Associated with Flavor Quality

**SUMMARY**—Explosion puffed dehydrated potatoes may develop a characteristic off-flavor during puffing. An objective method, based on the analysis of headspace vapor by GLC, was developed to measure peak heights of components associated with this off-flavor. Ground potatoes and an internal standard, ethylbutyrate, were added to boiling water, and the mixture was equilibrated for 10 min at 98°C. A vapor sample was then withdrawn and analyzed chromatographically on a Carbowax 20M packed column at 100°C using an inlet splitter. Heights of peaks corresponding to 2-methylpropanal plus acetone, 2-methylbutanal plus 3-methylbutanal, hexanal, and ethylbutyrate were determined and peak ratios calculated. The method was found to be precise, accurate, and rapid. Comparisons of a number of potato samples by sensory evaluation and the objective method showed that the intensity of the off-flavor is associated with the heights of the 2-methylpropanal plus acetone and 2-methylbutanal plus 3-methylbutanal peaks.

### INTRODUCTION

EXPLOSION PUFFED dehydrated potatoes may develop a characteristic off-flavor during puffing which has at least two major flavor notes, one being described as scorched and the other as resembling wet fur or laundry. Both are distinct from the rancid flavors which may also develop in this product on storage. The intensity of the "puffing" off-flavor varies with the processing conditions and can be reduced by various modifications of the process (Cording et al., 1968).

Research was undertaken to determine the identity and origin of the "puffing" off-flavor and to eliminate this defect through process modification. To accomplish these aims, an objective method for the determination of flavor quality in explosion puffed dehydrated potatoes was required.

Investigations of the flavor of boiled potatoes by Self et al. (1963) resulted in the identification of 11 volatile compounds, a number of which may arise from the Strecker degradation of amino acids (Casey et al., 1965). Buttery and Teranishi (1963), using direct vapor injection gas-liquid chromatography, found that three of these volatile compounds, 2-methylpropanal (2MP) and 2- and 3-methylbutanal (2MB and 3MB) were present in the vapor above reconstituted potato granules which had been stored under conditions favoring nonenzymatic browning. Using a modification of the direct vapor injection technique, Filipic (1967) demonstrated that these same compounds were present in explosion puffed dehydrated potatoes and that their concentration was related to the intensity of the "puffing" off-flavor.

The present work describes the development and application of this objective method for the determination of flavor quality in explosion puffed dehydrated potatoes.

### EXPERIMENTAL

#### Preparation of potato samples

15g of ground (20 mesh) dehydrated potatoes were added to 300 ml preboiled distilled water at 98–100°C in a 500 ml Erlenmeyer flask which was immersed to a constant depth in a boiling water bath, mixing in the flask being provided by a magnetic stirrer. Immediately after the addition of the potato sample, the flask was stoppered with a No. 7 rubber stopper through which was inserted a 90 × 21 mm glass tube closed at the top with a serum cap. The glass tube was heated to a wall temperature of approximately 105°C by a heater tape to minimize condensation. The flask-stopper assembly was vented to the atmosphere with a 24 gauge 3/4 in. hypodermic needle inserted in the serum cap.

Exactly 1 min after the flask was stoppered, 1 ml of a freshly prepared aqueous solution containing 40–50 ppm ethylbutyrate, used as an internal standard, was injected through the serum cap into the potato slurry using a 1 ml syringe and a 20 gauge 6 in. hypodermic needle.

Within 5 min the potato slurry attained a constant temperature of 98°C.

Exactly 10 min after the flask was stoppered, a vapor sample was removed for analysis.

#### Syringe technique

A 2.5 ml Hamilton Gas Tight syringe, insulated with asbestos tape and fitted with a Hamilton 2 in. chromatograph type needle (KF 72822), was heated to approximately 80°C in a vacuum oven. The syringe was removed from the oven 15 sec before the vapor sample was taken, and the needle was inserted through the serum cap in the stopper assembly. Approximately 2.2 ml of vapor was withdrawn, held in the syringe for 5 sec and then injected back into the flask without removing the needle. A second 2.2 ml vapor sample was then withdrawn and held in the syringe for 10 sec. The volume was adjusted to 2.0 ml, the needle was withdrawn from the serum cap, and the vapor was injected immediately into the gas chromatograph.

#### Gas-liquid chromatography

Vapor samples were analyzed with a Perkin-Elmer Model F-11 Gas Chromatograph using a 9 ft 1/8 in. stainless steel column containing 20% Carbowax 20M on 60/80 acid washed Chromosorb W. The oven temperature was set

to 100°C and the injection temperature to a setting of 5 (265°C). An inlet splitter (Perkin-Elmer Split Needle Assembly N 72822) was used to give a split ratio of approximately 3 and a helium flow rate through the column of 22 ml/min; air and hydrogen flow rates to the flame ionization detector were more than 200 and 24.5 ml/min, respectively. The flame ionization amplifier was set to a range of 10. The amplifier output was recorded using a Clevite Brush Mark 250 Recorder set at 100 mv with a chart speed of 0.5 min/division. Chromatograms were recorded for approximately 10 min after which no further peaks were observed.

With this procedure it was possible to perform as many as 18 analyses in an 8-hr day.

#### Mass spectral analysis of headspace vapor components

The previously described procedure for sample preparation and analysis were modified as described below to facilitate the mass spectral analysis of headspace vapor components. A slurry consisting of 50g ground explosion puffed dehydrated potato in 300 ml H<sub>2</sub>O in a 500 ml Erlenmeyer flask was held at room temperature for 3 hr, then saturated with anhydrous Na<sub>2</sub>SO<sub>4</sub> and equilibrated in a boiling water bath for 1 hr. A 2 ml headspace sample was injected into an F & M 810 Gas Chromatograph and separated on a 12 ft 1/8 in. stainless steel column containing 15% Carbowax 20M on 80/100 Chromosorb W at 100°C using a helium flow rate of 20 ml/min and a thermal conduc-

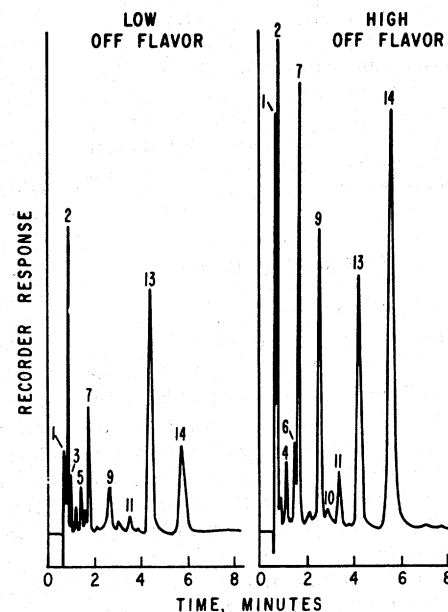


Fig. 1—Headspace vapor analysis of explosion puffed dehydrated potatoes having low and high off-flavor levels.

tivity detector at maximum sensitivity. The gas chromatograph was coupled to a CEC 103 Mass Spectrometer using a stainless steel helium separator at the interface. Chromatograms obtained by this procedure were found to be similar to those obtained by the standard procedure.

#### Analysis of aldehyde solutions

Standard curves of peak height vs aldehyde concentration in aqueous solution were obtained by adding different volumes of freshly prepared standard 2MP, 2MB, and 3MB solutions to 300 ml of preboiled distilled water at 98–100°C in place of the potato sample and then following the procedure described previously without exception. Concentrations were chosen to produce peak heights similar to those obtained with potatoes having an intense "puffing" off-flavor.

Similar curves of peak height vs. aldehyde concentration in potato were obtained by adding different volumes of the same aldehydes to boiling slurries of dehydrated potato having a low level of the puffing off-flavor immediately after the slurry (15g/300 ml distilled water) had been prepared. The previously described procedure was then followed.

All analyses were performed in triplicate or quadruplicate.

#### Sensory evaluations

Samples of dehydrated potatoes were reconstituted in boiling water (30g dice/500 ml H<sub>2</sub>O) in covered saucepans; explosion puffed products were simmered for 5 min while conventionally dried potatoes were simmered for 20 min. Reconstituted samples were examined in the cooking water by a panel of three expert tasters who are experienced in the evaluation of potato products and sensitive to the off-flavors produced by puffing. Members of the panel independently evaluated coded samples for aroma and flavor and then discussed their observations to arrive at an over-all judgment of off-flavor intensity.

A trained panel of 15 tasters were also used to validate the objective headspace vapor analytical procedure. Tasters were screened for sensitivity to the off-flavor; those selected for the panel were trained by repeated tasting of fresh boiled potato and dehydrated potato samples varying in off-flavor intensity. Panelists were asked to assess the off-flavor level in coded samples of puffed and conventionally dried potatoes using a nine point scale ranging from 0 (no off-flavor) to 8 (very high off-flavor level).

## RESULTS & DISCUSSION

#### Analysis of potato samples

Headspace vapor analysis of potato samples differing in flavor quality produced chromatograms showing at least 15 peaks (Fig. 1). Peak 7, identified by retention time and mass spectroscopy as 2MP plus acetone, and peak 9, identified by these procedures as 2MB and/or 3MB, were found to be major components in potato samples having the "puffing" off-flavor. Peak 14, identified by retention time and mass spectroscopy as n-hexanal, was present as a major component in rancid potato samples. These results are in agreement with those of Buttery and Teranishi (1963). The size of other peaks

Table 1—Precision of potato headspace vapor analysis.

Component <sup>a</sup>	Peak height (cm) or ratio					
	Good potato			Poor potato		
	Mean	Std. Dev.	Coeff. Var.	Mean	Std. Dev.	Coef. Var.
2MP + acetone	2.75	.42	15.2	9.11	.651	7.15
2MB + 3MB	1.02	.15	14.5	5.92	.474	8.00
Hexanal	1.98	.36	18.3	7.56	1.06	14.00
(2MP + acetone)/EB <sup>b</sup>	.504	.054	10.7	2.04	.247	12.1
(2MB + 3MB)/EB <sup>b</sup>	.187	.020	10.8	1.32	.122	9.24
Hexanal/EB <sup>b</sup>	.360	.018	5.09	1.68	.056	3.33
Number of replicates		5			5	

<sup>a</sup>2MP = 2-methylpropanal; 2MB = 2-methylbutanal; 3MB = 3-methylbutanal; EB = ethylbutyrate.

<sup>b</sup>Ratio of individual peak heights to the height of the ethylbutyrate peak for each analysis.

Table 2—Regression analysis of peak heights and peak ratios vs aldehyde concentrations in aqueous solutions and in potato slurry.<sup>a</sup>

Aldehyde	Sample	Regression coefficient and standard error <sup>b</sup>					
		Peak Height			Peak Ratio		
		a	b	Sy	a	b	Sy
2-Methylpropanal	Aqueous soln.	0.26	1.16	0.417	0.13	0.782	0.312
	Potato slurry	.99	1.28	.250	.52	.695	.096
3-Methylbutanal	Aqueous soln.	.06	1.02	.341	.07	.627	.166
	Potato slurry	.55	1.01	.463	.35	.499	.068
2-Methylbutanal	Aqueous soln.	-.03	.933	.538	0	.592	.140
	Potato slurry	.68	1.06	.357	.32	.609	.118

<sup>a</sup>Prepared from potato sample having low off-flavor level, 2-MP peak height = 0.97 cm; 2-MB plus 3-MB peak height = 0.69 cm.

<sup>b</sup>Regression coefficients and the standard error of the estimate in y (Sy) were calculated for the equation  $y = a + bx$  where y = peak height (or ratio); a = y intercept; b = slope; and x = aldehyde conc. (μg/ml).

showed little or no relationship to flavor defects in the potato samples.

#### Effect of water vapor

Preliminary headspace vapor analyses, carried out without the inlet splitter, frequently produced chromatograms in which the hexanal peak was greatly sharpened; in addition, the retention time of this and nearby peaks was slightly reduced. Experiments with wet and dry samples of potato headspace vapor and the vapor above various aldehydes demonstrated that this effect was due to the injection of large and variable amounts of water vapor in headspace samples. Only those compounds having retention times close to that of water were subject to the effect. Similar results were reported by Perry (1966) for n-alkanes in the presence of water and by Wills and Palmer (1967) for esters and some aldehydes and 2-alkanones in the presence of water.

Since the water vapor effect was sufficiently great and unpredictable to impede any quantitative peak height measurements of hexanal or other subject compounds, attempts were made to minimize

the effect by changing the injection and/or chromatographic techniques. The water vapor effect could be completely eliminated by introducing the inlet splitter into the chromatographic system, thereby decreasing the amount of water vapor reaching the column, and by concurrently decreasing the attenuation of the flame ionization amplifier to compensate for the smaller sample size.

#### Precision of headspace vapor analysis

To obtain satisfactory precision, it was necessary to standardize the procedure rigorously, especially the method of vapor sampling, and to introduce an internal standard. Ethylbutyrate was selected as the internal standard since it was found to be sufficiently water soluble and stable for this purpose and since its retention time under the conditions of the analysis corresponded to a gap in the potato headspace vapor chromatograms.

Examples of the precision of the method are given in Table 1. The conversion of peak heights to peak ratios, using the internal standard, was found to be especially advantageous with the 2MB

Table 3—Comparison of objective and subjective evaluations of off-flavor level in dehydrated potatoes.

Panel	Sample	Process	Peak ratio <sup>a</sup>		Sensory evaluation of off-flavor level <sup>b</sup>
			2MP + acetone	2MB + 3MB	
			EB	EB	
Expert 1	334 wo	Puffed	2.03	1.41	Moderate-strong
	338 wo	Puffed	1.66	2.00	Moderate-strong
	334 w	Puffed	0.50	0.19	Low
	337 w	Puffed	0.83	0.58	Low
Expert 2	338 wo	Puffed	1.66	2.00	Moderate-strong
	342 wo	Puffed	2.24	1.89	Moderate
	344 wo	Puffed	1.60	0.63	Moderate
	344 w	Puffed	0.54	0.20	Low
	344	Conventional	0.48	0.10	Absent
Expert 3	359 wo	Puffed	1.32	1.15	Moderate-strong
	359 w	Puffed	1.13	0.94	Moderate
	358 wo	Puffed	0.82	0.56	Low-moderate
	359	Conventional	0.32	0.11	Absent
Trained	359 wo	Puffed	1.32	1.15	3.25 (Moderate)
	359 w	Puffed	1.13	0.94	2.07 (Slight)
	359	Conventional	0.32	0.11	0.14 (Absent)

<sup>a</sup>2MP = 2-methylpropanal, 2MB = 2-methylbutanal, 3MB = 3-methylbutanal, EB = ethylbutyrate.

<sup>b</sup>Numerical scores obtained from the trained panel of 15 tasters are on a 9 point scale ranging from 0 (no off-flavor) to 8 (very high off-flavor).

plus 3MB peak and the hexanal peak since coefficients of variation for these ratios tended to be substantially lower than for the individual peak height.

#### Accuracy of headspace vapor analysis

An indication of the accuracy of the headspace vapor analysis was obtained from the results of analyses of aqueous aldehyde solutions and potato slurries to which aldehydes had been added. In all cases, a linear relationship was found between peak height and aldehyde concentration over the range of aldehyde concentrations employed: 0–0.5 µg/ml of solution or slurry (Table 2).

The slopes of these curves, calculated by linear regression, were similar for aqueous solutions and potato slurries. Slopes for 2MB and 3MB were similar and slightly lower than those obtained with 2MP. Calculated intercepts (aldehyde concentration – 0) for potato slurries to which aldehydes were added corresponded well to independent measure-

ments of peak heights in slurries containing no added aldehydes.

Another aspect of the accuracy of the procedure is the rate of equilibration of the headspace vapor composition. This is determined by the rate of rehydration of the potato sample, the geometry of the system, the temperature of the potato slurry, the extent of condensation in the system and the degree to which air in the system is vented. Analyses of potato headspace vapor sampled after 5, 10, 15, 30, 45, and 60 min showed that equilibration occurred within 5–10 min after the addition of the ground potato to the flask; little or no change occurred in the peak heights thereafter.

#### Application of headspace vapor analysis

The headspace vapor analysis was applied to many samples of explosion puffed and conventionally dehydrated potatoes which were also subjected to sensory evaluation by the expert panel. These samples represented a number of

different experimental batches in which the raw material and processing conditions were varied. The sensory and analytical data summarized in Table 3 were obtained at three different panel sessions held during a 1 yr period. Also included in Table 3 are the results of an evaluation of 3 samples by the larger trained panel.

These data show a positive association between the intensity of the off-flavor produced by puffing and the peak heights of the branched chain aldehydes. Differences reported by the trained panel are significant at  $P < .05$  using Duncan's multiple range test (Le Clerg, 1957). The association appears to be more consistent with 2 MB + 3MB than with 2MP, probably since the latter peak also contains acetone, a normal volatile component of fresh potato (Self et al., 1963). No attempt has been made to quantify the association between peak height and off-flavor intensity because of the difficulty in comparing sensory data obtained at different panel sessions. This might be feasible if a standard source of the off-flavor could be prepared and evaluated by the panel at each session.

#### REFERENCES

- Buttery, R.G. and Teranishi, R. 1963. Measurement of fat autoxidation and browning aldehydes in food vapors by direct vapor injection gas-liquid chromatography. *J. Agr. Food Chem.* 11: 504–507.
- Casey, J.C., Self, R. and Swain, T. 1965. Factors influencing the production of low boiling volatiles from foods. *J. Food Sci.* 30: 33–34.
- Cording, J. Jr., Sullivan, J.F. and Talley, F.B. 1968. Eastern Utilization R&D Div., USDA, Philadelphia. Personal communications.
- Filipic, V.J. 1967. Eastern Utilization R&D Div., USDA, Philadelphia. Unpublished data.
- Le Clerg, E.L. 1957. "Mean separation by the functional analysis of variance and multiple comparisons." USDA, ARS 20 (3).
- Perry, S.G. 1966. Displacement effect of water in gas chromatography. *J. Chromatog.* 23: 468–470.
- Self, R. and Swain, T. 1963. Flavour in potatoes. *Proc. Nutr. Soc.* 22: 176–182.
- Wills, R.B.H. and Palmer, J.K. 1967. The effect of water on the retention times of alcohols and esters. *J. Chromatog.* 30: 208–210.

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